

TABLE I—COMPARATIVE DISTILLATIONS OF KELP, DOUGLAS FIR AND OAK

No. of run	Mois- ture	GRAMS OF MATERIALS OBTAINED	Less mois- ture	Set- tled tar	Char- coal	Gas by diff.	Total time of distil- lation Hrs.	% of dry wt. of material	Acid Methyl as alcohol 100%	Set- tled tar
ON 1 KG. OF KELP (<i>Macrocystis pyrifera</i>)										
3	116	290	174	..	465	245	3	..	..	..
6	116	255	139	..	465	280	2.5	..	..	..
9	116	265	149	..	500	235	12	..	..	..
11	116	262	146	48	485	253	3	0.34	..	5.4
12	116	283	167	41	512	205	3.75	0.49	Av.	4.6
13	116	277	161	60	472	251	4	0.28	0.14	6.8
14	116	242	126	37	487	271	4	0.28	..	4.2
15	116	217	101	30	515	268	8	..	..	3.4
23	116	277	161	60	485	238	4	0.49	0.20	6.8
24	116	305	189	55	460	235	8	0.58	0.18	6.2
ON 1 KG. OF DOUGLAS FIR										
16	190	414	224	60	260	326	3	1.5	0.7	7.0
17	190	424	234	80	276	300	2.5	..	0.7	10.0
25	190	450	260	100	300	250	4	1.6	..	12.0
ON 1 KG. OF OAK SAWDUST										
18	366	550	184	45	200	250	4	2.9	1.1	7.0
19	313	424	111	60	230	346	3.5	2.6	1.3	9.0
20	313	412	99	37	215	373	4.5	2.5	1.2	6.0

REMARKS ON DETAILS OF DISTILLATIONS

RUN No. 3—Retort at red heat 1.5 hrs.		RUN No. 18—8.35 A.M.	
RUN No. 6—Heated rapidly to red heat		Pyrometer readings	
RUN No. 9—Very slow; low heat; 12 hrs.		9.05 A.M. 170° C.	
		gases burn	
RUN No. 13		9.15 A.M. 160° C.	
		9.15 200	
		large watery	
		10.05 270	
		distillate	
		11.50 290	
Started at 1.20 P.M.		12.30 P.M. 530	
		9.30 200	
		10.35 220	
		11.15 280	
Pyrometer readings		RUN No. 20—1.05 P.M.	
1.45 P.M. 120° C.		Pyrometer readings	
2.00 160		1.40 P.M. 160° C.	
2.30 200		2.40 200	
3.10 220		3.20 250	
		5.25 500	
4.05 240		12.25 P.M. 500	
gases slightly		RUN No. 15—9.00 A.M.	
combustible		9.30 A.M. 140° C.	
4.30 360		9.50 170	
gases burned		10.45 190	
steadily		12.00 M. 200	
4.50 420		2.00 P.M. 220	
5.10 500		2.15 290	
no more distillate		3.20 390	
		4.30 400	
		4.45 530	

from the gases produced by the oak and fir. Turrentine gives the following data regarding the gases evolved in his experiment:

ANALYSES OF GAS SAMPLES FROM DESTRUCTIVE DISTILLATION OF KELP (MACROCYSTIS)—(TURRENTINE)

Sample No. Pyrometer	1 320° F.	3 480° F.	5 590° F.	7 900° F.
CO ₂	80.0	70.0	44.0	20.2
Illuminants.....	2.0	4.0	10.0	3.3
O ₂	0.5	1.5	0.8	0.5
CO.....	10.5	8.5	6.7	4.0
H ₂	..	10.6	23.5	32.0
Methane.....	2.88	4.8	4.4	7.6
Nitrogen (by diff.).....	4.12	0.6	10.6	32.4
Total per cent.....	100.00	100.00	100.00	100.00
Wt. per cu. ft.....	0.106040	0.094	0.074150	0.057600
Cal. value.....	107.45	196.70	352.05	282.54

The charcoal residue was very soft and had a dull luster. A leaching experiment was made, using 2860 g. of charcoal, with an excess of distilled water. The solution was evaporated and three fractions crystallized out as is shown in Table II.

TABLE II—LEACHING AND FRACTIONATION

Frac- tion No.	Vol. of mother liquor	Wt. of dry salts Grams	Per cent of K ₂ O in salts	I in salts	REMARKS
1.....	2600 cc.	450	58.0	0.03	Pure white crystals
2.....	1600 cc.	283	55.6	0.08	Nearly pure
3.....	860 cc.	252	47.3	0.17	white crystals
Mother liquor ..	..	368	19.1	1.46	..

Per cent K₂O in 3 fractions combined = 54.6 = 86.8 per cent KCl.
Per cent of total K₂O recovered in 3 crystallizations = 88.
Per cent of total I in mother liquor = 87.

By passing the weak liquors over fresh portions of charcoal repeatedly it was found possible to leach out practically all of the potash and iodine with minimum quantities of water.

SUMMARY

1—Comparative laboratory distillations of kelp (*Macrocystis pyrifera*) with oak and fir were made. The data obtained did not indicate that the kelp distillates would have a commercial value.

2—Most of the potash may easily be recovered from the charcoal as a high-grade product.

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NOTE ON IDENTIFYING AMIDO-H-ACIDS

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There are no published methods of identifying the 2-amido-H-acid, the 7-amido-H-acid and the 2,7-diamido-H-acid. H-acid is 1,8-amido-naphthol-3,6-disulfo acid. Ability to detect and differentiate these acids is frequently necessary for industrial purposes in obtaining light on the mode of making and the composition of certain coal-tar dyes.

The methods of identification described below were worked out with known H-acid and other materials and were successfully applied to disputed dyes; they are offered with confidence as to accuracy and conclusiveness so far as these three sulfo-acids are concerned. Corresponding mono- and di-amido derivatives of acids isomeric with, or analogous to, H-acid have not been similarly examined. Whether conflict exists in that regard has not been determined; this will call for further work by others. This note is not at all a notice of pre-emption but an invitation to others to enter this field. An analysis of the products worked on was not made; reliance for the constitution of these substances is placed solely upon the history and behavior of the materials employed.

The 2-amido-H-acid was made from H-acid by coupling it in hydrochloric solution with diazotized paranitranilin (one molecule), reducing and separating the acid product from the para-phenylene diamine; the 2,7-diamido-H-acid was made from the foregoing coupling product and a further molecule of diazotized paranitranilin, coupling in alkaline (carbonate), solution and treating this result as outlined above; 7-amido-H-acid was made from the coupling product of H-acid and diazotized paranitranilin (one molecule), coupled alkaline (carbonate); this product was reduced and separated as outlined above.

There is nothing new in the coupling methods used. The reducing and separation methods may be new. The general procedure was as follows:

Mix one gram of each of these coupling products with 10 cc. water, heat to 60° C., add one gram zinc dust thoroughly suspended in 5 cc. water, shake thoroughly, add 5 cc. of a 36° Bé. sodium bisulfite solution, shake thoroughly, gradually raise to a boil and maintain at boiling until further color-change does not take place; filter rapidly, cool, add 6 cc. hydrochloric acid (sp. gr. 1.16) to cooled filtrate; cool in a freezing mixture to 0° C. or below and maintain at that temperature until solid no longer separates out (this may take from half hour to 2 or 3 hours); filter upon paper through a Gooch; drain thoroughly; wash carefully with small amounts of saturated salt solution until drip is colorless.

or almost so; wash with as little 95 per cent ethyl alcohol as possible (3 to 4 cc.), and follow with a wash of 1 or 2 cc. of ether; remove the solid from the filter paper and dry on a watch-glass at 90° C. The solid obtained is the amido-H-acid of the coupling product used. The same procedure applies to dyes from H-acid; if the dye-amount taken be less than one gram the proportion of reagents used should be altered to correspond.

The three identification tests used were as follows:

I—Boil a fraction of a milligram of the free acid with a few drops of 40 per cent caustic soda solution, dilute with 1 cc. water and note color produced; boiling the diluted solution may at times be necessary.

II—Place a fraction of a milligram of the free acid into 2 or 3 drops conc. H_2SO_4 (sp. gr. 1.84) and warm until it begins to turn violet; add one or two drops 0.5 per cent sodium nitrite solution; cool; dilute with 0.5 cc. water; cool (if a brown opalescence or turbidity appears here start all over again and do not heat quite so high); neutralize largely with 40 per cent caustic soda, finish neutralizing and make alkaline with slight excess saturated carbonate of soda solution; note color change.

III—Dissolve a fraction of a milligram of the free acid in one drop of saturated carbonate of soda solution, using heat if need be; add one drop concentrated hydrochloric acid, dilute with water to 0.5 cc., heat to boiling and cool; place a drop of this on good white filter paper; add right on top of it a drop or two of good hydrogen peroxide solution; when the color-development has reached its maximum, add a drop of 40 per cent caustic soda solution, preferably right on top of the other drops. Note color changes.

The behavior of these acids is tabulated as follows:

Test	2-Acid	7-Acid	2,7-Acid
I.....	Yellow or brown	Green	Violet going to blue
II.....	Blue-red	Blue-red	Yellow or brown
III H_2O_2	Brown or yellow	Violet to red	Blue
NaOH.....	Red	White or cream colored	Red to violet

By suitably combining these tests it is possible to detect all three of these acids in mixtures of 90 : 5 : 5 of any combination; with care, 200 mg. of H-acid-dye will answer to carry out this separation and all three of these tests. The colors produced by Test III can be photographed, *e. g.*, on a Lumière plate and the colors so preserved for reference; they are not stable, as such.

Condensation with phenanthrene-quinone is not satisfactory, calling for much time and care, and frequently failing where it should succeed; moreover, the amounts needed are very much larger than in the tests described; 2-amido-H-acid gives such a condensation product which is yellow, soluble in carbonate of soda and is precipitated therefrom by common salt and dissolves in concentrated sulfuric acid with a corn-flower-blue color; the 2,7-diamido-H-acid does not yield such a condensation product under any practicable condition nor does the 7-amido-H-acid.

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INDIGOTIN CONTENT OF SOME JAPANESE INDIGOS¹

By SHINJIRO SATO

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The analyses given below were made on commercial samples from the Province of Awa, where nearly all the Japanese indigo is produced. The remarkable features of the results are the low indigotin content and high ash. These are not surprising, however, when considered in relation to the methods of production, which have been modified but little since the introduction of indigo culture into Japan over two hundred years ago.²

In the native process the dried leaves of the *Polygonum tinctoria* are heaped on dirt floors, then thoroughly moistened with water and allowed to ferment. The piles are turned over from time to time, the whole process requiring about three months. The fermented mass, called "sukumo," is pounded up in large wooden mortars with mallets, then mixed with water and left to harden. The resulting cake is pressed and cut into cubes, called "tamas" ("Tama," Japanese word for "gem") in which form it is put on the market.

The above method requires much time and labor and yields a product of low indigotin content, since there is no extraction to separate the dye from the fiber of the plant. An extraction method applicable to Japanese conditions has been perfected by Dr. N. Nagai.³ Although the method requires less time and labor than the older process and produces a superior indigo, it has not yet been generally adopted.

METHOD OF ANALYSIS

To test out the methods of analysis pure indigotin was first prepared, starting with Indigo S Pdr. furnished by the Badische Co. This was purified according to the method of Mönlau and Zimmermann,⁴ by dissolving in 100 parts glacial acetic acid and 4 parts sulfuric acid, then hydrolyzing by diluting with water. The precipitated indigotin was washed, dried at 110°, and nitrogen determined by the Kjeldahl method.

	Found	Theoretical	
N	10.62 per cent	10.69 per cent	Indigotin 99.35 per cent

The method adopted for extracting and estimating indigotin is a modification of Rawson's procedure⁵ in which he extracted indigotin by sulfonation and titrated with $N/50$ permanganate. The original method was modified by its author⁶ and later by Bertheil and Briggs,⁷ whose procedure was adhered to exactly in the following analyses. The above methods for preparation of pure indigotin and for analysis of commercial indigos have been alternately criticized and defended.⁸

RESULTS OF ANALYSIS

Ash and indigotin are calculated on weight of dry

¹ Partial abstract of a thesis presented to the Faculty of the State College of Washington in part fulfillment of the requirements for the B.S. degree.

² History of Awa Indigo. (Published in Japanese.)

³ Nagai, Lectures on Awa Indigo. (Published in Japanese.)

⁴ Zeits. Farb. Text. Chem., **10** (1903), 189.

⁵ J. Soc. Dyers and Col., **1** (1885), 74.

⁶ J. Soc. Chem. Ind., **35** (1906), 730.

⁷ Ibid., **18** (1899), 251; **25** (1906), 734.

⁸ Ibid., **26** (1907), 4, 182, 1172, 1174.